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(Total 3 pages)

54. Title of Invention	Method of removing organic films
21. Application No.	Showa 48-34544
22. Date of Filing	March 28, 1973 (Showa 48)
43. Patent Laid-open Date:	November 26, 1974 (Showa 49)
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Claims

1. A method of removing the organic film adhered to a substrate, that removes said organic film while supplying ozone to said organic film.

Detailed explanation of the invention

The present invention relates to a method of removing organic films.

In technologies for photolithographically processing semiconductor wafers, a method that dips the wafer to be processed to which a photoresist film is adhered, in a heated sulfuric acid solution has been known as a method of removing the photoresist film after development.

However, according this method, the ability of the solution to oxidize the photoresist film is not always sufficient, and consequently, the photoresist film cannot be completely etched away.

Therefore, a solution that is made by adding a powerful oxidant, such as K₂Cr₂O₇, to sulfuric acid has been tried. However, because K₂Cr₂O₇ is toxic and becomes a pollution source, waste liquid disposal becomes costly, resulting in high manufacturing costs.

¹ ILC Note – An alternative way of reading this name is "Susukida".

The present inventor performed photoresist processing of a film on a Si substrate during the manufacture of a linear IC and tried to use a plasma ash method for removing the photoresist film. However, as shown in Figure 2, a problem of deteriorating linear IC characteristics (h_{FE} degradation) was encountered. The cause of this problem is presumed to be as follows. Since the metals, e.g., aluminum, Sn, etc., contained in the photoresist cannot be completely removed with this method, applying a heating process (e.g., diffusion) to the semiconductor device from this state sinters the aforementioned metals into the semiconductor.

Therefore, a decision was made to add a hydrogen peroxide solution, rather than the aforementioned $K_2Cr_2O_7$, to the sulfuric acid solution in order to enhance its etching ability.

With this method, the oxygen in the nascent state generated when the unstable hydrogen peroxide solution decomposes reacts violently with the photoresist, making its removal easier.

However, according this method, because the etching effect declines as time elapses after the hydrogen peroxide solution is added, the sulfuric acid and hydrogen peroxide solution must be replenished continuously, making the operation inconvenient and the material costs high.

Therefore, the present invention was conceived to enable constant supply of oxygen in the nascent state into sulfuric acid solution. Accordingly, the objective of the present invention is to provide an etching method that completely removes organic films and at the same time that does not have the (pollution) problem of waste liquid disposal or characteristics degradation.

In order to achieve the aforementioned objective, the present invention has a basic configuration of a method of removing the organic film adhered to a substrate, that removes said organic film while supplying ozone to said organic film.

The present invention is explained below with reference to a working example.

Figure 1 shows a working example of the present invention.

Numerical 1 denotes a tank; 2 is a sulfuric acid solution (25 ~ 100%) placed inside tank 1; 3 is an ozone generator provided outside; 4 is a pipe for supplying ozone from the ozone generator into solution 2; 5 is a nozzle provided in pipe 4; 6 is a jig on which to place a semiconductor wafer; and 7 is a semiconductor wafer to which the photoresist removal process is to be applied.

Supplying ozone O_3 from ozone generator 3 into sulfuric acid solution 2 inside tank 1, thereby generating oxygen in the nascent state inside the solution and increasing its oxidizing ability, enhances the ability to remove a photoresist, e.g., OMR81 or OMR83 (product names), and cleans the surface of semiconductor wafer 7.

Liquid temperature of between 40 and 150°C is ideal, and a 5-minute dip, for example, can completely remove the photoresist.

According to such a method, ozone O_3 supplied into the sulfuric acid solution and the oxygen in the nascent state generated from ozone O_3 react strongly with the photoresist, completely removing the photoresist.

The conventional method that uses H_2O_2 as the oxidant has a problem in that H_2O_2 must be constantly replenished, resulting in inconvenience and high costs. In contrast, the present working example can use

a commercially available ozone generator to constantly supply ozone using ordinary air as the raw material, thus eliminating the cost of the oxidant.

Furthermore, because the method according to the present invention does not use a toxic substance, a pollution problem stemming from waste liquid disposal is eliminated. Additionally, since the photoresist can be completely removed, the characteristic degradation that occurs with the use of a plasma ashing method is also prevented.

The table below summarizes the results of the evaluation of various etching methods according to various criteria. O means that there were no problems at all; Δ means there were some problems; and X means there were serious problems.

Processing method	Waste liquid disposal	Ease of use	Safety	Etching ability	Effects on characteristics
H ₂ SO ₄ K ₂ Cr ₂ O ₇	X	O	O	O	O
Plasma ashing method	O	O	O	O	X
H ₂ SO ₄	O	Δ	O	Δ	O
H ₂ SO ₄ H ₂ O ₂	O	Δ	O	O	O
J-100 (product name)	Δ	O	O	Δ	O
Present working example	O	O	O	O	O

(Note that J-100 is the name of a product that consists of a mixture of (1) phenol, (2) alkylbenzene mumhol(??) acid, (3) tetrachloroethylene, and (4) O-dichlorobenzene.)

As is clear from this table, the method in the present working example is the only one that does not have any problems in any of the five criteria, including waste liquid disposal, ease of use, etc.

Note that hydrochloric acid or sulfuric[sic] acid can also be used in place of sulfuric acid as the processing solution. Furthermore, since the effect of O₃ is great, the photoresist can be removed using water instead of an acid.

The present invention can be effectively used in all cases involving the removal of organic films from a substrate.

Brief explanation of the drawing

Figure 1 shows a working example of the present invention.

Figure 2 shows curves showing how h_{FE} deteriorates when a plasma ashing process is applied.

1 ... tank, 2 ... sulfuric acid solution, 3 ... ozone generator, 4 ... ozone gas supply pipe, 5 ... nozzle, 6 ... wafer placement jig, 7 ... wafer.



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Figure 1

Figure 2

Plasma ashing usage condition

Output: 400 W; Pressure: 2.5 Torr; Time: 10 minutes

O₂ flow rate: 300 cc/min (Wet O₂)

J-100 treatment

J-100 treatment

Ashing

Ashing

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001809247

WPI Acc No: 77-30226Y/197717
Removing organic phot resist film from silicon semiconductor wafer - by

contacting with inorganic acid & ln. and zone

Patent Assignee: HITACHI LTD (HITA)

Number of Countries: 001 Number of Patents: 001

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Main IPC	Week
JP 77012063	B	19770404					197717 B

Priority Applications (No Type Date): JP 7334544 A 19730328

Abstract (Basic): JP 77012063 B

The film adhered to the silicon wafer is contacted with inorganic acid soln. and simultaneously jetted with ozone.

The process is a photographic technique for removing photo-resist film from a silicon wafer after developing.

Derwent Class: G06; L03; U11; U12

International Patent Class (Additional): H01L-021/30

?

特許公報

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発明の数 1

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1

④有機被膜の除去方法

⑪特 願 昭48-34544

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⑬昭49(1974)11月26日

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⑤特許請求の範囲

1 基板に付着した有機被膜を除去する方法において、上記有機被膜にオゾンを供給しながら上記有機被膜を除去することを特徴とする有機被膜の除去方法。

発明の詳細な説明

この発明は有機被膜の除去方法に関する。

半導体ウエハの写真処理技術において、現像後フォトロジスト膜を除去する方法として、加熱された硫酸溶液中にフォトロジスト膜が付着した被處理ウエハを浸漬する方法が従来から知られている。

しかし、この方法によれば液のフォトロジスト膜に対する酸化能力が必ずしも充分でないためにフォトロジスト膜を完全に剥離できない欠点があつた。

そこで、強力な酸化剤である例えばK₂C₂O₇を硫酸に添加してつくつた溶液を使用して剥離することも試みられたが、K₂C₂O₇は毒性を有し公害原となる廃液処理に費用がかかり、製造費が高くつくことで問題があつた。

本願発明者は、リニアICの製造においてSi

基板上の被膜のフォトロジスト処理を行い、現像後のフォトロジスト膜除去にプラズマアツシヤー法の採用を試みたが、第2図に示すようにリニアICの特性劣化(hFEの低下)を生ずる問題があつた。これは、フォトロジストに含まれた金属、例えばアルミニウム、Sn等をこの方法では完全に除去できないことから、そのまま半導体素子に対して加熱処理(例えば拡散)を施した場合に上記金属が半導体内にシンターされることに起因するものと考えられる。

そこで、硫酸溶液に剝離性を強めるものとして前述のK₂C₂O₇に代え、過酸化水素水を添加使用することとした。

これによれば、不安定な過酸化水素水が分解して発生する発生期の酸素がフォトロジストと激しく反応するので、剝離し易くなる。

しかし、この方法によれば過酸化水素水を添加後時間の経過により剝離効果が減少し、次々と硫酸および過酸化水素水を補給する必要があるため作業上不便であるばかりでなく、材料費が高価格となる欠点があつた。

そこで、発生期の酸素を常時硫酸溶液内に低価格で供給できるようにするために本発明をなした。したがつて、本発明の目的は有機被膜を完全に除去し、且つ排液処理(公害)特性劣化の問題の生じないような剝離方法を提供することにある。

上記の目的を達成するための発明の基本的な構成は、基板に付着した有機被膜を除去する方法において上記有機被膜にオゾンを供給しながら上記有機被膜を除去することを特徴とするものである。

以下本発明を実施例により説明する。

第1図は本発明の一実施例を示すものである。

1は槽、2は槽1内に入れられた硫酸溶液(25~100%)、3は槽1の外部に設けられたオゾン発生装置、4はオゾン発生装置から溶液2内へオゾンを供給するための管、5は管4に設けられたノズル、6は半導体ウエハ載置用治具、

7はフォトレジスト分離処理が施される半導体ウエハである。

槽1内の硫酸溶液2中に、オゾン発生装置3よりオゾンO₃を供給することにより、溶液中において発生期の酸素Oを発生させ酸化能力を増進させることによりホトレジスト例えばOMR81、OMR83(商品名)の除去能力を向上させ半導体ウエハ表面7を清浄化する。

液温は40~150℃が好適で例えば5分間の長時間処理で、フォトレジストをきれいに除去することができる。

このような方法によれば、硫酸溶液中に供給されたオゾンO₃、およびオゾンO₃から発生される発生期の酸素Oが、フォトレジストと強力に反応し、フォトレジストが完全に除去される。

また、従来のH₂O₂を酸化剤として使用する方法によれば、そのH₂O₂を常時補給する必要があるので不便で材料費がかさむという問題があつたが、本実施例によれば市販のオゾン発生装置を使用することにより普通の空気を原料としてオゾンを常時供給することができ、酸化剤の原料費が不要である。

さらに、本発明方法によれば有毒物質を使用することがないので、排液処理による公害問題もなく、また、完全にフォトレジストを除去することができることからプラズマアツシヤー方法により除去した場合に生じた特性劣化の問題もない。

次の表は、各剥離方法を各観点から検討した結果をまとめたもので、○は全く問題のないこと、△は若干問題があること、×は非常に大きな問題のあることを示す。

処理方法	廃液処理	使い易さ	安全性	剥離能力	特性への影響
H ₂ SO ₄ , K ₂ Cr ₂ O ₇	×	○	○	○	○
プラズマアツシヤー法	○	○	○	○	×
H ₂ SO ₄	○	△	○	△	○
H ₂ SO ₄ , H ₂ O ₂	○	△	○	○	○
J-100 (商品名)	△	○	○	△	○
本実施例	○	○	○	○	○

(なお、J-100は商品名で、①フェノール、②アルキルベンゼンマムホール酸、③テトラクロールエチレン、④○ージクロルベンゼンを混ぜたもの)

この表からも明らかなように廃液処理、使い易さ等5つの観点からみて全く問題のないのは本実施例の方法だけである。

なお、処理用溶液として硫酸に代え塩酸あるいは硫酸を使用することもでき、また、O₃を用いたことによる効果の大きさから酸に代え水を用いてもフォトレジストの除去を行うことができるものである。

本発明は有機被膜を基板より剥離する場合のすべてに有効に適用できるものである。

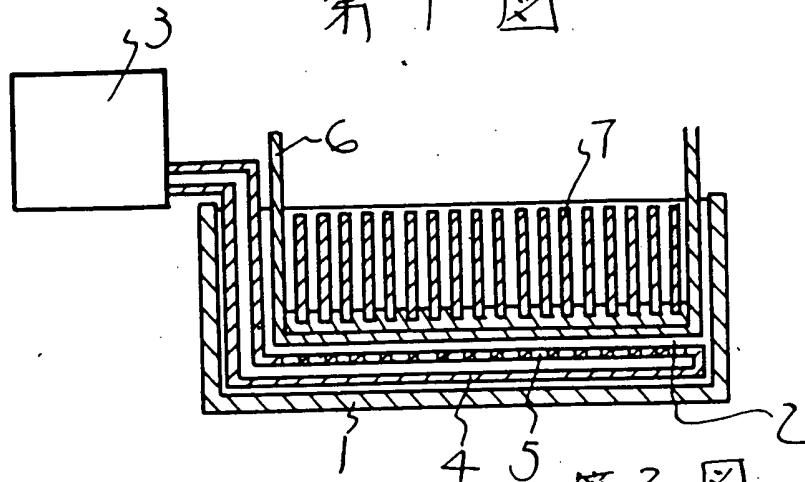
図面の簡単な説明

第1図は本発明の一実施例を示すものである。

第2図はプラズマアツシヤー処理をしたことによりhFEが低下することを示す曲線図である。

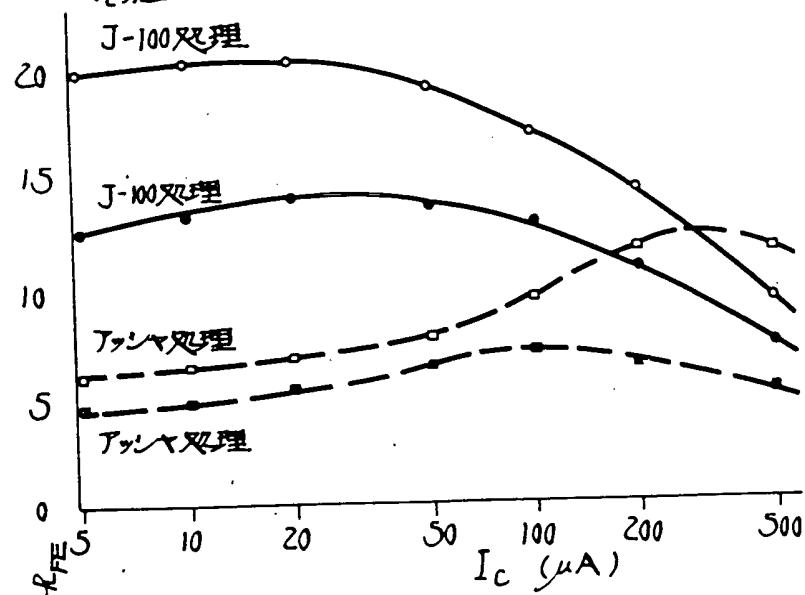
1……槽、2……硫酸溶液、3……オゾン発生装置、4……オゾンガス供給管、5……ノズル、35 6……ウエハ載置治具、7……ウエハ。

第1図



第2図

プラズマアッシャ使用条件
出力: 400W 壓力: 2.5 Torr, 時間10分
 O_2 流量: 300 cc/min (Wet O_2)



EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

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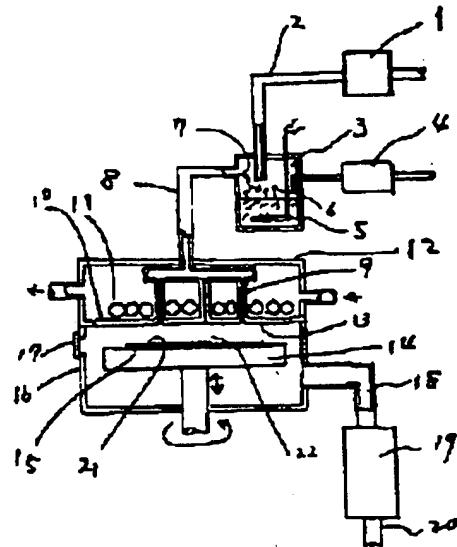
APPLICATION DATE : 29-03-91
APPLICATION NUMBER : 03065976

APPLICANT : HITACHI LTD;

INVENTOR : INADA AKIISA;

INT.CL. : H01L 21/304

TITLE : CLEANING METHOD



ABSTRACT : PURPOSE: To improve the ashing removal performance of an organic matter such as resist used as a mask for augmenting the throughput by a method wherein steam is sufficiently mixed with the ozone at a specific volume ratio, and the mixture is fed onto the surface of the object to be processed.

CONSTITUTION: The ozone produced by an ozone producer 1 is led in a steam feed vessel 3 through an A-piping 2. This steam feed vessel 3 is fed with pure water or hydrogen peroxide by a constant quantity feeder 4 with a heater A5 built therein to maintain the constant water temperature inside the vessel 3. This steam 6 evaporated from the water in the vessel 3 are carried by the ozone stream 7 is fed to multiple gas feed nozzles 9. At this time, the volume of the steam 6 added to the ozone is specified to exceed about 0.7 times of the ozone volume, and they are sufficiently mixed. Through these procedures, the removing rate can be accelerated up to the level exceeding 120% compared with the case not fed with the steam.

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